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(21)Application number : 11-021593 (71)Applicant : SHINSHU CERAMICS:KK

(22)Date of filing : 29.01.1999 (72)Inventor : SAKURADA TSUKASA

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## (54) ADHERENT TREATING AGENT

### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a printing ink capable of imparting excellent germicidal effects to paper products, cloth products, plastic products, etc., according to a simple method.

SOLUTION: This printing ink or coating material is obtained by mixing and kneading a colorant and a vehicle or a coating film-forming substance with a photocatalyst comprising a photoconductor powder and a metal powder and an adsorbent material such as apatite. The printing ink or coating material is used to form a desired pattern or a desired image on paper products, cloth products, plastic products, etc., to thereby adsorb and retain bacteria by the adsorbent material in the printing ink or coating material. Sterilization is carried out by photocatalytic actions with the semiconductor powder and metal powder. The paper products, etc., are suitable as, e.g. food packaging materials or medical materials.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the covering processing agent which can continue for a long period of time, and can demonstrate the sterilizing properties, the deodorization force, etc. which it excelled in base material front faces, such as a paper product, a cloth product, a plastic, and metal goods, by carrying out covering processing.

**[0002]**

**[the technique since \*\*]** Although we coexist with various bacteria in a general living environment, it is desirable to always annihilate bacteria harmful to the body also in it, and to hold a clarification environment, and especially the request is large in the hospital which holds many patients. Of course, according to spraying of a bacteria agent, a certain amount of effectiveness is securable, but although it is the bacteria object, it becomes harmful to the body on the contrary to sprinkle a germicide indefinitely to a living environment, and it is not desirable. Moreover, since it has resistance in an antibiotic in the case of MRSA (MESHICHIRIN resistance yellow staphylococcus) which has caused the problem of a hospital infection, big anxiety has been especially given to the patient after an operation to which the immunity force is falling, an old man, and the mother and child at the time of childbirth. And this is unsolvable depending on spraying of a mere germicide.

**[0003]** Therefore, although it becomes important to repeat carefully cleaning and wash as the after all most fundamental defecation approach, when holding a long-term medical-treatment person in domestic, the thoroughness is difficult, also in the hospital which has the special personnel, the thoroughness serves as a big economic burden, and it leads also to the burden rebounding upon a user.

**[0004]**

**[Problem(s) to be Solved by the Invention]** In order to solve the above problems, this invention person has proposed the sterilization adsorption functional object which comes to carry out thermal spraying of the mixture which contains adsorption components, such as optical semiconductive ceramics and an apatite, on a base material previously (refer to JP,6-254139,A). This sterilization adsorption functional object is the technique which could demonstrate outstanding sterilizing properties semipermanently and was moreover extremely excellent in the point of being harmless to the body.

**[0005]** Then, this invention aims at offering the covering processing agent which enables simpler utilization, maintaining outstanding sterilizing properties equivalent to said technique by carrying out expansion development of the technique given in JP,6-254139,A further.

**[0006]**

**[Means for Solving the Problem]** This invention offers the adherent for making an adsorption ingredient, and these photocatalysts and adsorption ingredient for adsorbing the photocatalyst which combined optical semi-conductor powder and metal powder, and the object processed according to a photocatalyst operation of bacteria, a smell, harmful matter, etc., and holding it as a means to attain the above-mentioned object, put to base material front faces, such as paper, cloth, and plastics.

**[0007]**

[Embodiment of the Invention] A scientific operation is made by the electrochemistry cel which the optical semi-conductor powder used for the covering processing agent of this invention is called a photocatalyst with combination with metal powder, uses one [ nothing and ] electrode as optical semiconductive ceramics for a photocatalyst operation depending on temperature in response to the fact that an optical exposure, and uses the electrode of another side as a metal.

[0008] As this optical semi-conductor powder, TiO<sub>2</sub>, CdS, CdSe, WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SrTiO<sub>3</sub>, and KNbO<sub>3</sub> grade can be mentioned. In this invention, it is scientifically stable, and it is approved also as a food additive, there is no sanitary problem, and TiO<sub>2</sub> which had that oxidization and reduction are the well-balanced ceramics and the crystalline form of anatase since acquisition was easy and it was cheap is desirable.

[0009] When good covering workability is taken into consideration, the particle size of these optical semi-conductor powder has desirable 0.01-2.0 micrometers, and its 0.3-0.6 micrometers are especially desirable, while it secures bigger surface area.

[0010] While becomes a pair and the metal powder used for the covering processing agent of this invention forms an electrode, as described above. As this metal powder, various metal powder, such as gold, silver, platinum, and copper, can be used. Since moisture is required as one of the indispensable elements for demonstrating a function with an original photocatalyst in the metal powder as a photocatalyst, platinum is the most desirable also in the metal powder described above from it being necessary for there to be no aging under existence of water and to be stable, but in consideration of profitability, said property is provided further, and it is harmless, and since it has disinfectant also in itself, silver is desirable.

[0011] The particle size of such metal powder has desirable 0.05-0.1 micrometers, when relation with optical semi-conductor powder is taken into consideration as a photocatalyst.

[0012] 1 - 55 weight section of metal powder is desirable to the optical semi-conductor powder 100 weight section, and the mixed rate of optical semi-conductor powder and metal powder has especially desirable 20 - 30 weight section, in order to demonstrate sterilization, a deodorization operation, etc. suitably.

[0013] The amount of adsorbents used for the covering processing agent of this invention is for adsorbing processing objects, such as a malodorous substance besides bacteria, a virus, and mold, and harmful matter, and holding them. One or more sorts chosen from the group which consists of ceramic powder, such as an apatite (apatite), a zeolite, or sepiolite, activated carbon, and a silk fibre inclusion as this adsorption ingredient can be mentioned, and these can be used combining two or more sorts if needed.

[0014] Here, as an apatite, the hydroxyapatite [calcium<sub>10</sub>(PO<sub>4</sub>)<sub>5</sub>(OH)<sub>2</sub>] which adsorbs protein, such as bacteria, a virus, and mold, selectively is desirable. Moreover, as a silk fibre inclusion, a thing, a gel object, etc. which were fabricated to granularity besides silk fibre powder are contained.

[0015] When good covering workability is taken into consideration, the particle size of these adsorption ingredients (in the case [ Silk fibre inclusion ] of powder) has desirable 0.001-1.0 micrometers, and its 0.01-0.05 micrometers are especially desirable, while it secures bigger surface area.

[0016] An adsorption ingredient has desirable 1 - 50 weight section to the optical semi-conductor powder 100 weight section, and the mixed rate of optical semi-conductor powder and an adsorption ingredient has especially desirable 10 - 30 weight section, in order to demonstrate sterilization, a deodorization operation, etc. suitably.

[0017] The covering processing agent of this invention mixes each above-mentioned component, is made to \*\*\*\* optical semi-conductor powder and metal powder into an adsorption ingredient, and can obtain them. Such a covering processing agent of this invention can be used being able to distribute dispersion media, such as water and an organic solvent, although it can be used even if it remains as it is. It is made to cover by applying to a base material front face as it is on the occasion of the activity, and also the interior can also be made to contain as a bulking agent of other ingredients.

[0018] This invention can be replaced with the covering processing agent of such a mode, and can be used as the printing ink or the coating which is the activity gestalt of the covering force over a

processing object, and the others [ give / the ornament effectiveness etc. / further ] as an object. [0019] In addition to the photocatalyst and adsorption ingredient which consist of optical semi-conductor powder and metal powder, the printing ink which is other one gestalt of this invention contains coloring matter and a vehicle at least as an adherent on which a photocatalyst is made to put to a base material front face, and contains other components if needed.

[0020] As coloring matter, colors, such as the oil color besides what is generally used as coloring matter of printing ink, for example, an inorganic pigment, and an organic pigment, and a disperse dye, can be mentioned.

[0021] As a vehicle, semi-drying oil, such as drying oil, such as an oil, for example, the linseed oil etc., and soybean oil, Nondrying oil, such as castor oil, can be mentioned. Resin, for example, rosin, Natural resin, such as denaturation rosin and a BIRUSO night, or a natural resin derivative, phenol resin, Alkyd resin, xylene resin, a urea-resin, melamine resin, polyamide resin, Acrylic resin, an epoxy resin, ketone resin, petroleum resin, vinyl chloride resin, polyvinyl acetate, urethane resin, chlorination polypropylene, chlorinated rubber, cyclized rubber, a cellulosic, and reactant resin can be mentioned, and, in addition to this, a plasticizer can be mentioned.

[0022] Moreover, as other components, the low component of a natural low or synthetic wax, a drying agent, a dispersant, a wetting agent, a crosslinking agent, a gelling agent, a thickener, an anti-skinning agent, a stabilizer, a delustering agent, defoaming material, a color separation inhibitor, a photopolymerization initiator, an antimold, etc. can be mentioned.

[0023] There is no special thing in the blending ratio of coal of each of these components, and it can apply the same blending ratio of coal as the printing ink usually marketed to it.

[0024] In order that the sum total loadings of the optical semi-conductor powder in printing ink, metal powder, and an adsorption ingredient may demonstrate an operation of sterilization, deodorization, etc. and may secure moderate printing nature, its 3 - 55 % of the weight is desirable among the printing ink whole quantity, and its 15 - 35 % of the weight is especially desirable.

[0025] Especially the gestalt and class of such printing ink are not restricted, can be used as paste ink, solvent ink, or non-solvent ink, and can apply them as lithography ink, Toppan Printing ink, gravure ink, screen-stencil ink, intaglio-printing ink, and special printing ink. In order to attain the object of this invention most effectively also in these, the ink for screen-stencil, such as screen ink for papers, screen ink for plastics, screen ink for glass, and screen ink for cloth, is desirable.

[0026] Next, the coating which is one gestalt of further others of this invention is explained. In addition to the photocatalyst and adsorption ingredient which consist of optical semi-conductor powder and metal powder, a coating contains a paint film formation component and a dispersant, and contains other components if needed.

[0027] As a paint film formation component, synthetic resin, such as a cellulosic, phthalic resin, phenol resin, ARUGIDO resin, amino alkyd resin, acrylic resin, an epoxy resin, urethane resin, vinyl chloride resin, silicone resin, a fluororesin, an emulsion, and water soluble resin, can be mentioned, and, in addition to this, vegetable drying oil can be mentioned.

[0028] As a dispersant, a petroleum solvent, an aromatic solvent, an alcohols solvent, an ester solvent, ketones, the Cellosolve system solvent, water, etc. can be mentioned. In addition, in making it powder coatings, the solvent as a dispersant becomes unnecessary.

[0029] Moreover, the special function pigment represented by corrosion prevention pigments, such as extenders, such as organic pigments, such as inorganic pigments, such as a pigment, for example, a titanium dioxide, the chrome yellow, red ocher, chromic oxide, and carbon black, Hansa yellow, a nova palm orange, the Quinacridone violet, and a copper phthalocyanine, precipitated calcium carbonate, a barium sulfate, talc, clay, and white carbon, Zinc chromate, strontium chromate, phosphoric-acid zinc, and aluminium phosphate, can be mentioned as other components.

[0030] Furthermore, the drying agent as an auxiliary material besides the above-mentioned component aiming at grant of paint film desiccation acceleration nature, A polymerization catalyst, the wetting agent aiming at dispersibility amelioration of a pigment, a pigment agent, a flooding inhibitor, A pigment sedimentation inhibitor, the thickener aiming at fluid accommodation of a coating, a

CHIKISOTORO pick agent, It hangs down and a plasticizer besides a stop agent, the leveling agent aiming at adjustment of the painted surface, a defoaming agent, a crawling inhibitor, and a floating inhibitor, an anti-skinning agent, an electrostatic-coating assistant, an excoriation inhibitor, an antiblocking agent, an ultraviolet-rays inhibitor, a resist, antiseptics, an antifungal agent, etc. can be blended.

[0031] There is no special thing in the blending ratio of coal of each of these components, and it can apply the same blending ratio of coal as the coating usually marketed to it.

[0032] In order that the sum total loadings of the optical semi-conductor powder in a coating, metal powder, and an adsorption ingredient may demonstrate an operation of sterilization, deodorization, etc. and may secure moderate paintwork, its 3 - 55 % of the weight is desirable among the coating whole quantity, and its 15 - 35 % of the weight is especially desirable.

[0033] Especially the method of application of such a coating is not restricted, and can apply approaches, such as brush coating, air spray painting, airless spray painting, electrostatic coating, powder coating, electrodeposition coating, curtain flow coating, and roll coating.

[0034] In the covering processing agent of this invention, in the case of (refer to drawing 1 ), bacteria, WISURU, mold, etc., bacteria, WISURU, mold or a malodorous substance, harmful matter, etc. are simultaneously annihilated to the rear stirrup by carrying out adsorption maintenance with an adsorption ingredient first according to the photocatalyst operation by the optical semi-conductor and metal powder which receive an optical exposure, and, in the case of a malodorous substance etc., it is decomposed. Furthermore, also in a case of what is not adsorbed, growth prevention, the evasion effectiveness, etc. are acquired according to a photocatalyst operation. The resistance value change by illuminance change of a photocatalyst is shown, it is shown that the resistance of a photocatalyst (optical semi-conductor) changes with the illuminances of light, and, as for drawing 1 , it turns out that migration of an electron takes place by the exposure of light.

[0035] Moreover, the covering processing agent of this invention can carry out the same photocatalyst operation as a carrier beam case for an optical exposure in the general life temperature requirement expected on the earth, even when not receiving an optical exposure at all (refer to drawing 2 ). That is, drawing 2 shows the resistance value change by the temperature change of a photocatalyst, and according to this, change of temperature shows that an optical semi-conductor operates.

[0036] Furthermore, in order to disassemble the protein which constitutes the bacteria by which the adsorption ingredient was adsorbed, a virus, mold, etc. and to disappear, said effectiveness is maintained semipermanently, without decreasing with time.

[0037] Although especially the covering area on the base material of the covering processing agent of this invention is not restricted and changes with applications, the above-mentioned effectiveness can usually be acquired 20% or more to the total surface area of a base material by making it cover so that it may become 40 - 60% preferably. Moreover, while it can reduce the dues of a covering processing agent, since applying the approach which are in the condition which carried out the covering processing agent like a grid pattern or polka dots, and homogeneity was made to distribute, for example, and a processing side is made to cover on the occasion of covering processing can demonstrate homogeneity, effective adsorption, and a photocatalyst operation, it is desirable.

[0038] Although bacteria, mold, etc. like the conditions of high-humidity/temperature and propagate, the photocatalyst in the covering processing agent of this invention demonstrates the function effectively especially under such a high-humidity/temperature condition. Therefore, when it takes into consideration including the sterilization component in the covering processing agent of this invention being a non-eluted system ingredient, the covering processing agent of this invention is an object which enables application in the very large range as \*\*\*\* and the growth control technique of the living thing containing bacteria, mold, etc.

[0039] The covering processing agents containing modes, such as printing ink of this invention and a coating, are various configurations, and can give sterilization, the deodorization effectiveness, etc. by making it cover on the base material which consists of various ingredients, such as paper, timber, cloth, plastics, a metal, and concrete. Moreover, since the decorative effectiveness by printing a desired pattern

and an image can also be given, it can use for the various applications which need them, and can use also for the application which cannot expect an optical exposure further.

[0040] By making paper cover, for example, wrapping, such as wrapping for [ various ] food preservation, and a package bag, Outside wallpaper, a shoji, a sliding door, and furniture by being able to use as charges of housing lumber, such as a flare ingredient, also being able to perform utilization by in addition to this making a paper raw material contain as a sizing compound, and making cloth (fiber) and woolen stuff cover bedding (a sheet, a quilt cover, and a blanket cover --) clothes, a mask, a curtain, and at large It can use as various products or those material of construction, such as various coverings (various chair coverings, floor cushion covering, etc.), such as a pillow case, a tablecloth, a carpet, a towel, and a handkerchief, and can use as ingredients, such as a filter for air scouring, or a filter for backwashing by water. Moreover, it can use also as an antifouling paint which prevents adhesion of aquatic organisms, such as acorn shells in the object for paint of a building and the structure, the object for paint of various products, a ship, a pons, a landing bridge, etc., a serpula, and a sea mussel.

[0041] This invention is not limited by these although an example explains this invention in more detail below.

[0042] First, the mixed powder which mixed the silver powder (particle size of 0.1-0.8 micrometers) 10 weight section and the hydroxyapatite (particle size of 0.05-0.8 micrometers) 10 weight section was prepared to the TiO<sub>2</sub> (particle size of 0.1-1.0 micrometers) 100 weight section.

[0043] Next, 998g of they and said mixed powder were kneaded by the mixer, using urethane system resin as 2g of inorganic pigments, and a vehicle. In addition, the blending ratio of coal of the mixed powder in the ink whole quantity could be 10 % of the weight. The container was filled up with this kneading object with the restoration machine, and the screen ink for cloth was obtained.

The sterilization trial to MRSA-A, MRSA-B, and Pseudomonas aeruginosa was performed by the following approach using the screen ink for cloth obtained in the example of trial 1 example 1.

(1) Trial cloth example cloth : all over the whole surface side of a protein nonwoven fabric, the screen ink for cloth obtained in the example 1 was applied so that thickness might be set to about 5 micrometers, and it was used as the example cloth.

[0044] Cloth for objects: The non-processed acrylic nonwoven fabric was used as the cloth for objects (the germicidal action is not reported about an acrylic nonwoven fabric).

(2) The fungus liquid containing sample offering bacillus MRSA-A ( $7.8 \times 10^{10}$ -/ml), MRSA-B ( $7.3 \times 10^7$ -/ml), and Pseudomonas aeruginosa ( $3.8 \times 10^9$ -/ml) was used.

(3) A total of seven circles (diameter of 4.8mm) were drawn on the front face of two test-method example cloth and two cloth for objects in ink without disinfectant, and each circle was made into the circle for observation 10 minutes and 20 minutes, 1 hour, 3 hours, 6 hours, and 24 hours after [ next ].

[0045] Next, it applied 0.2ml of fungus liquid of MRSA-A, MRSA-B, or Pseudomonas aeruginosa at a time in the circle for every cloth, extended uniformly by FUWABU, and was left in the laboratory. In addition, FUWABU sterilizes by hot air and each cloth carried out ultraviolet ray pasteurization beforehand for 24 hours.

[0046] Next, after predetermined time progress, the inside of the circle which corresponds for every cloth was carefully wiped off 5 times by the swab, and the bacillus which extracted and extracted the bacillus was put into the test tube which poured in sterilization bouillon 3ml. Then, fungus liquid was continuously diluted up to ten to 105 times.

[0047] Next, 1ml was taken from each dilution fungus liquid, and these were moved to a petri dish of ten sheets different, respectively. Then, the nutrient agar medium was added in each petri dish, after stirring so that it may become homogeneity, it cultivated at 35 degrees C for 48 hours, and number of microorganism was counted. The count of number of microorganism chose four things of the available factor which is easy to count from the petri dish of ten sheets, and took the average. A result is shown in a table 1.

[0048]

[A table 1]

時 間	MRSA-A ( $7.8 \times 10^{10}/\text{ml}$ )		MRSA-B ( $7.3 \times 10^7/\text{ml}$ )		绿膿菌 ( $3.8 \times 10^9/\text{ml}$ )	
	実施例布菌数	対照用布菌数	実施例布菌数	対照用布菌数	実施例布菌数	対照用布菌数
直 後	$4.5 \times 10^3$	$2.5 \times 10^6$	$2.9 \times 10^3$	$7.8 \times 10^6$	$1.3 \times 10^6$	$5.5 \times 10^6$
10分	$1.8 \times 10^3$	$2.1 \times 10^6$	$2.1 \times 10^3$	$5.3 \times 10^6$	$1.0 \times 10^6$	$4.2 \times 10^6$
30分	$9.4 \times 10^2$	$2.1 \times 10^6$	$1.7 \times 10^3$	$5.7 \times 10^6$	$6.1 \times 10^3$	$1.5 \times 10^6$
1時間	$8.6 \times 10^2$	$1.6 \times 10^6$	$1.5 \times 10^3$	$7.1 \times 10^6$	$3.0 \times 10^3$	$1.4 \times 10^6$
3時間	$7.6 \times 10^2$	$1.4 \times 10^6$	$1.4 \times 10^3$	$4.8 \times 10^6$	$2.9 \times 10^3$	$8.0 \times 10^4$
6時間	$6.9 \times 10^2$	$1.9 \times 10^6$	$2.6 \times 10^3$	$4.4 \times 10^6$	$8.4 \times 10^2$	$6.0 \times 10^4$
24時間	$7.0 \times 10^2$	$8.0 \times 10^2$	$3.8 \times 10^3$	$3.9 \times 10^6$	0	$7.0 \times 10^3$

[0049] When a covering processing agent was used as printing ink a passage clear from the result of a table 1, the outstanding bactericidal effect was shown to MRSA and Pseudomonas aeruginosa. Since this trial is performed in a laboratory and the special optical exposure is omitted, as shown in drawing 1 and drawing 2, this bactericidal effect is accepted to be what was discovered by light and both the factors of temperature, especially the thermal factor. Therefore, a hospital infection can also be prevented while being able to keep a medical supply normal, whenever it applies this printing ink to a medical supply.

[0050]

[Effect of the Invention] Demonstrating the covering processing agent of this invention can be continued semipermanently, without decreasing the outstanding sterilization, a deodorization operation, etc. according to the absorption by the adsorption ingredient, and the photocatalyst operation by optical semi-conductor powder and metal powder. \*\* et al. [ furthermore, ] -- \*\* -- an operation can fully be demonstrated, even when there is no optical exposure.

[0051] Moreover, since the covering art is simple, the covering processing agent of this invention can be used in a broad field.

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[Translation done.]